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## Separation of Americium from Lanthanides by Purified Cyanex 301 Countercurrent Extraction in Miniature Centrifugal Contactors

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### Abstract

In order to further test the actinides/lanthanides separation performance by Cyanex 301 extraction, a countercurrent extraction experiment was carried out in the present work. The separation process consisted of 7-stage extraction, 3-stage scrubbing and 4-stage stripping. 14 miniature centrifugal contactors were installed in glove box for the experiment. The feed solution from TRPO process, mainly consisting of 4.4M HNO<sub>3</sub>,  $\sim 3.7 \times 10^8$  Bq Am-241, 0.02M lanthanides,  $\sim 120$  ppm Mo and 100 ppm Fe, was pretreated by the following procedures: denitrating to 0.2M HNO<sub>3</sub> by formic acid, adjusting pH to 2 by 8M NaOH, removing most Fe<sup>3+</sup> by 0.2M Cyanex 301-kerosene cross-flow extraction, and then adjusting pH to 3.5 by 1M NaOH. About  $5.6 \times 10^8$  Bq Pm-147 was added into the feed solution to trace lanthanides during the experiment. The experiment lasted for 9 hours with a feed flow rate of 30 ml/h. The results show that 99.95% Am was separated from lanthanides and only 0.1% lanthanides were extracted together with Am. 99.3% Am and 96.6% Pm were stripped from load Cyanex 301 by 1.0M HNO<sub>3</sub>, respectively.

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**Keywords:** Americium; lanthanides; separation; Cyanex 301, centrifugal contactor

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### 1. Introduction

In the partitioning of high level waste (HLW), fission product lanthanides (FPLns) always enter the Am (Cm) stream. For example, Am (Cm) and FPLns are stripped together by 5.5M HNO<sub>3</sub> in the TRPO process<sup>[1,2]</sup>. However, lanthanides should be further separated from Am(Cm) for the transmutation of actinides because some

lanthanides will become neutron poison in the transmutation due to high neutron-absorption cross-sections. The effective separation of Am from FPLNs is a key problem in the "partitioning-transmutation" nuclear fuel cycle.

On the other hand, it is difficult to separate trivalent Am from lanthanides because they have similar physical and chemical properties in aqueous solution. Some extractants containing soft donor S or N have been found to have a high selectivity for trivalent actinides<sup>[3-8]</sup>. Among N-donor ligands, BTP(2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridine) is outstanding one<sup>[9,10]</sup> and the improved molecule BTBP(6,6'-(5,6-dialkyl-1,2,4-triazin-3-yl)2,2'-bipyridine) showed very excellent separation performance in acidic media<sup>[11,12]</sup>. CyMe<sub>4</sub>-BTBP was successfully tested in the SANEX process<sup>[13]</sup>. Among S-donor ligands, Cyanex 301, which contains ~80% bis(2,4,4-trimethylpentyl)dithiophosphinic acid (HBTMPDTP), has been proved able to separate Am from lanthanides effectively. The purified Cyanex 301, i.e. HBTMPDTP, can effectively separate Am from lanthanides with a extraction separation factor of >1000<sup>[7,14]</sup>. In the present work, a countercurrent extraction separation of americium from lanthanides by purified Cyanex 301 was carried out in miniature centrifugal contactors.

## 2. Experimental

### 2.1. Reagents and analysis methods

Cyanex 301 was produced by Cytec Inc. and was purified as described in reference [7]. 240<sup>#</sup> hydrogenated kerosene, from Jinzhou petroleum refinery, China, was redistilled and the fraction between 180°C and 220°C was collected as the solvent. The mixture of <sup>241</sup>Am and lanthanides is the 5.5M HNO<sub>3</sub>-stripping fraction from TRPO process which partitioned the simulated power HLW. It contains ~4.4M HNO<sub>3</sub>, lanthanides, <sup>241</sup>Am, little amount of Fe, Mo, and so on. <sup>147</sup>Pm was added into the feed to trace the lanthanides easily. All the other reagents used were of analytical grade.

Through  $\alpha/\beta$  discrimination, <sup>241</sup>Am and <sup>147</sup>Pm were measured by ultra low level liquid scintillation QUANTULUS 1220 with Ultima Gold™ AB as the scintillation cocktail (0.1ml sample and 5ml cocktail). The pH value of aqueous phases was measured by PHS- pH meter.



Fig. 1 The battery of miniature centrifugal contactors

## 2.2. Procedures

The original feed containing Am-241 and lanthanides was 4.4M HNO<sub>3</sub>-stripping stream from TRPO process. Before separation, the feed was denitrated by formic acid to 0.8M HNO<sub>3</sub> at 95°C, adjusted to pH 2 by 8M NaOH, and then treated by 0.2M Cyanex 301 extraction to remove Fe, Mo. After this, <sup>147</sup>Pm in 0.1M HNO<sub>3</sub> was added into the feed and the pH of the mixture was adjusted to 3.5 by 1M NaOH. Fig. 1 shows the battery of centrifugal contactors, which consists of 14-stage 10mm annular miniature centrifugal contactors developed at INET.

The separation process was determined based on the previous work.<sup>[15]</sup> Fig. 2 gives the schematic flowsheet, which consists of 7-stage extraction, 3-stage scrubbing and 4-stage stripping. The holdup in each stage was about 5ml. The feed, scrubbing solution, stripping solution and solvent were pumped into the centrifugal contactors by syringe pumps.

The outlet samples were collected after 9h operation. The aqueous and organic phases of each stage were sampled after stopping the contactors. The experiment was carried out at ambient temperature.

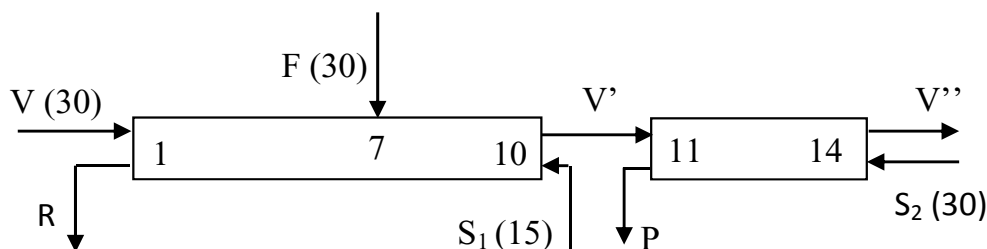


Fig. 2 Schematic flowsheet of Am separation from lanthanides by Cyanex 301 extraction

Where, the numbers in ( ) are the flow rates in ml/h.

F: feed,  $1.09 \times 10^6$  Bq/ml <sup>241</sup>Am +  $2.47 \times 10^6$  Bq/ml <sup>147</sup>Pm + 0.02M lanthanides + 0.8M NaNO<sub>3</sub>, pH=3.5

P: Am product

R: aqueous raffinate

S<sub>1</sub>: scrubbing solution, 0.1M NaNO<sub>3</sub>, pH=3.5

S<sub>2</sub>: stripping solution, 1.0M HNO<sub>3</sub>

V: 0.5M Cyanex 301-kerosene with a saponification of 2mol%

V': loaded organic phase

V'': spent organic phase

## 3. Results and discussion

Table 1 lists the pH of the raffinate (R) at different times. The results indicate that the cascade extraction experiment reached the stationary state after 7 hours.

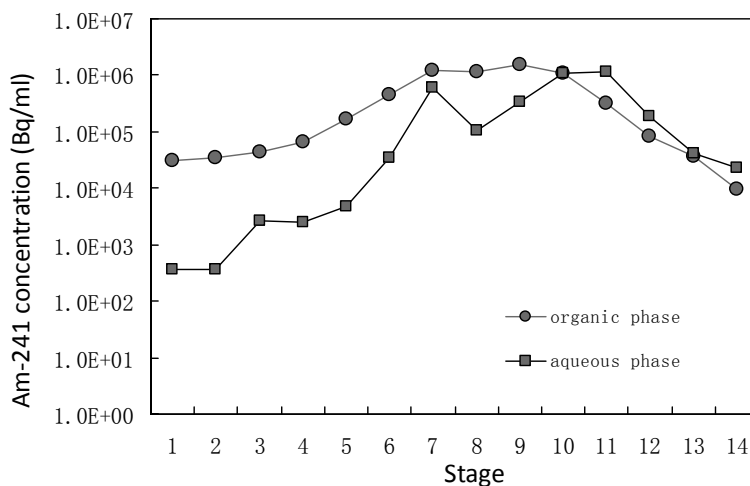
Fig. 3 and Fig. 4 give the concentration profiles of <sup>241</sup>Am and <sup>147</sup>Pm in two phases. The extraction percentage of <sup>241</sup>Am is 99.95%. The extraction behaviors of lanthanides is reasonably considered the same as <sup>147</sup>Pm, so the estimated extraction percentage of lanthanides is 0.1%. The separation of Am from lanthanides is about 2000 and the separation of lanthanides from Am is 980. The stripping percentages are 99.3% for <sup>241</sup>Am and 96.6% for <sup>147</sup>Pm, respectively. According to Boussier et al<sup>[16]</sup>, the Am transmutation requires a minimum mass ratio of Am

to fission products lanthanides near to 1:1. Therefore, the co-extracted FPLns is required <1.4% for the typical feed originated from the commercial reprocessing. In the present work, a much lower lanthanides extraction achieved the mass ratio of Am to lanthanides in the product P of 1.6:1, which can meet the above transmutation requirement.

Table 1 The evolution of pH in the raffinate

experimental time (h)	pH
1	4.70
2	4.18
3	4.01
4	4.05
5	4.45
6	4.41
7	4.32
8	4.33
9	4.34

Between 1.0M HNO<sub>3</sub> and 0.5M Cyanex 301-kerosene, the distribution ratio of Am is less than 0.01, which implies >99% <sup>241</sup>Am stripping each contact. However, the cascade stripping performance is not satisfied. The distribution ratios are 0.27~0.85, much higher than expected. No remarkable improvement could be made by adjusting the phase ratio, nitric acid concentration of stripping and the rotary speed of centrifugal contactor. Reducing the flow rate of two phases could obviously enhance the stripping of Am. Thus, the possible reason is that the single efficiency of contactor is very low because of short residence time of two phases and slow stripping reaction. Better stripping performance requires more residence time of two phases through changing the structure of contactor or reducing the flow rate.

Fig. 3 <sup>241</sup>Am concentration in each centrifugal contactor

In this work, the material balance (defined as 100×total outlet content/total inlet content) was found to be 105% for <sup>241</sup>Am and 99.6% for <sup>147</sup>Pm.

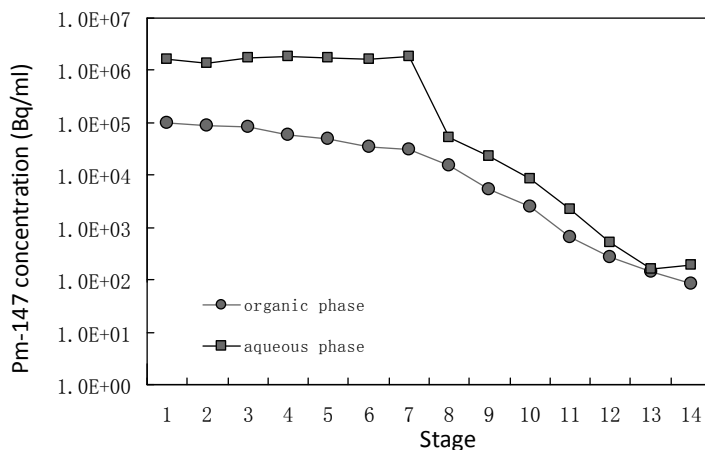


Fig. 4  $^{147}\text{Pm}$  concentration in each centrifugal contactor

Fig. 5 shows the pH values of aqueous phase in the extraction section. It can be seen that the pH decreased from stage 1 to feed stage, increased after feed, and then decreased. This phenomenon was possibly caused by the extraction and back extraction of lanthanides. During extraction, the distribution ratio of Am is better to be  $>1$  in order to avoid the accumulation of Am. So, the controlling of aqueous pH is very important. However, it is not easy to control the aqueous pH in the extraction of little amount of Am. More effective methods are needed to control the pH profile in Cyanex 301-based system.

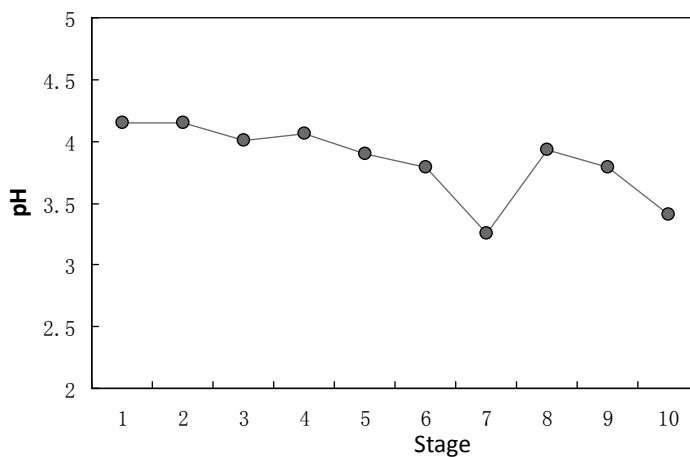


Fig.5 The aqueous pH in the extraction section

#### 4. Conclusions

The results show that Am and lanthanides have been well separated from each other by purified Cyanex 301 extraction in the centrifugal contactors. The separation of lanthanides from Am can meet the requirement of Am transmutation. In the future, it is necessary to study the stripping behavior of Am from Cyanex 301 and develop more effective method to control the aqueous pH in the extraction.

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